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"RESEARCH ON THE SOLUBILITY OF LEAD SULPHATE ^{IN} LEAD ACCUMULATORS (STORAGE
BATTERY)" (Report No 3)

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(360) "Research on the Solubility of Lead Sulphate ^{IN} Lead

Accumulator (Report No 3):

"The Solubility Sulphate Solutions"

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INTRODUCTION

Sulphates of alkali metals or alkali-earth metals in aqueous solution are used as "formation solutions" of lead accumulator plates; therefore the solubility of lead sulphate must influence the nature and capacity of the plates after "formation". This study completely covers solubility in the following four systems (Reports 1 and 2 treat solubility in sulfuric acid solution. 1943, No 46, Pp 1022 - 1024):

1. Concentration from zero to saturation in solutions of $(\text{NH}_4)_2\text{SO}_4$; Na_2SO_4 ; MgSO_4 .
2. Two-component solutions of 3N/liter: $(\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{SO}_4$; $\text{Na}_2\text{SO}_4 - \text{H}_2\text{SO}_4$; $\text{MgSO}_4 - \text{H}_2\text{SO}_4$.
3. The following system with 4N/liter: sulphate concentration $(\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{SO}_4$.
4. System where K_2SO_4 is added to battery electrolyte and $\text{K}_2\text{SO}_4 - \text{H}_2\text{SO}_4$ used as the "formation" solution.

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Bibliography

Data on the solubility of lead sulphate was indicated in the bibliography of Report I. Subsequent results are inserted for reference.

Test Methods

Methods used in the following tests are identical in very respect to those mentioned in Report I. Reagents used were acids tested with H_2S to ascertain the presence of heavy metallic elements which show a colored precipitate.

Results of Measurement1. $(NH_4)_2SO_4$ Solution (30°C)

Concentration		PbSO ₄ solubility in mg/liter		
N/kg.H ₂ O	N/liter	Supernatant method (skimming)	filtration method	average
0.52	0.5	6.4	6.8	6.6
1.05	1.0	9.8	9.6	9.7
1.58	1.5	12.9	12.9	12.9
2.15	2.0	16.6	16.6	16.6
2.74	2.5	17.5	17.5	17.5
3.34	3.0	15.8	15.9	15.9
3.91	3.5	14.2	14.1	14.2
4.65	4.0	12.2	-	12.2
4.65	4.0	10.4	10.1	10.2
4.65	4.0	10.0	10.0	10.0
6.04	5.0	9.5	9.1	9.3
8.83	6.7	7.5	7.0	7.3

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These values generally agree with those of Huybrechts and Ramelot (18°C) for lower concentrations.

solubility of PbSO_4 in
 $(\text{NH}_4)_2\text{SO}_4$ solutions

Our results (30°C)

Huybrechts and Ramelot (18°C)

Concentration of $(\text{NH}_4)_2\text{SO}_4$ (N/kg. H_2O)

2. Na_2SO_4 Solution (30°C)

Concentration		PbSO_4 solubility in mg/l		
N/kg. H_2O	N/liter	superatant method (skimming)	filtration method	average
0.51	0.5	5.7	5.7	5.7
1.02	1.0	9.5	9.2	9.4
2.08	2.0	14.3	14.2	14.3
3.13	3.0	26.1	26.5	26.3
3.13	3.0	26.1	26.1	26.1
4.53	4.2	28.6	-	28.6

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Solubility of PbSO_4 in Na_2SO_4 solution

Our results (30°C)

Huybrechts and Ramelot (18°C)

Concentration of Na_2SO_4 (N/kg. H_2O)

Huybrechts' and Ramelot's values (at 18°C) are about the same; more accurately speaking, their temperature was lower but solubility was somewhat larger.

3. MgSO_4 Solution (30°C).

Concentration		PbSO_4 's solubility in mg/liter		
N/kg. H_2O	N/liter	supernatant method (skimming)	filtration method	average
0.50	0.5	5.0	4.2	4.6
1.00	1.0	6.4	6.0	6.2
2.02	2.0	10.0	10.0	10.0
2.54	2.5	7.7	7.3	7.5
3.06	3.0	5.5	-	5.5
3.06	3.0	5.6	5.5	5.6
3.60	3.5	5.2	5.2	5.2

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4.14	4.0	6.8	6.8	6.8
4.14	4.0	7.1	-	7.1
5.78	5.5	6.0	6.0	6.0
5.78	5.5	6.1	6.0	6.1

Solubility of PbSO_4 in MgSO_4 solution

Measurement temperature 30°C

Concentration of MgSO_4 (N/kg. H_2O)

Note the unique appearance of two maximums in the curve.

4. K_2SO_4 solution (30°C)

The solubility of K_2SO_4 at normal temperatures does not exceed 1.3 N/liter.

The solubility of PbSO_4 in K_2SO_4 solution is very slight and difficult to determine on the colorimeter. Therefore, we prepared a PbS-sol solution with 16-cm liquid layer in a Nessler tube and compared it with the standard solution.

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Concentration		Solubility of PbSO_4 in mg/liter Colorimetrically compared in Nessler's tube
N/kg. H_2O	N/liter	
1.03	1.0	0.1
0.76	0.75	0.1
0.51	0.5	0.1

The solubility of PbSO_4 in K_2SO_4 solution

Our results (30°C)

Huybrechts and Ramelot (18°C)

Concentration of K_2SO_4 (N.kg. H_2O)

K^+ is similar to NH_4 and Na , but surprisingly enough the solubility of PbSO_4 is very slight. This small value is in agreement with Huybrecht's value.

5. Aqueous solution of the $(\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{SO}_4$ system (30°C)

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A). SO_4 concentration: 3.00 N/liter

(NH ₄) ₂ SO ₄ : H ₂ SO ₄ Molecular proportion	solubility of PbSO ₄ in mg/liter		
	supernatant method (skimming)	filtration method	average
100 : 0	16.0	16.1	16.1
100 : 0	15.8	15.9	15.9
99 : 1	-	-	-
90 : 10	15.6	15.6	15.6
70 : 30	14.4	14.4	14.4
60 : 40	11.2	11.1	11.2
50 : 50	10.7	10.5	10.6
40 : 60	10.2	10.1	10.2
30 : 70	8.6	8.6	8.6
20 : 80	8.3	8.1	8.2
10 : 90	7.6	-	7.6
1 : 99	-	-	-
0 : 100	6.5	6.6	6.6
0 : 100	6.7	7.1	6.9
0 : 100	7.1	6.8	7.0

B) SO_4 concentration: 4.00 N/liter

solubility of PbSO ₄ in mg/liter		
supernatant method (skimming)	filtration method	average
10.4	10.1	10.2
10.0	10.0	10.0
10.1	10.1	10.1
11.2	11.2	11.2
13.3	13.6	13.4
-	-	-
9.5	10.0	9.7
8.0	-	8.0
-	-	-
-	-	-
7.1	-	7.1
5.7	-	5.7
5.4	5.4	5.4
-	-	-
-	-	-

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Two-component H_2SO_4 - $(\text{NH}_4)_2\text{SO}_4$ system
 The solubility of PbSO_4 in an aqueous solution (at 30°C)

$(\text{NH}_4)_2\text{SO}_4$: H_2SO_4 mo/ratio

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6. Aqueous solution of $\text{Na}_2\text{SO}_4 - \text{H}_2\text{SO}_4$ (at 30°C)
 SO_4 concentration: 3.00 N/liter

The solubility of PbSO_4 in an aqueous solution of
 $\text{Na}_2\text{SO}_4 - \text{H}_2\text{SO}_4$

Na_2SO_4 ; H_2SO_4 mo/ratio

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Concentration, molecular ratio	solubility of PbSO_4 in mg/liter		
	supernatant method (skimming)	filtration method	average
100: 0	26.1	26.5	26.3
100:0	26.1	26.1	26.1
99: 1	20.3	-	20.3
90 :10	21.5	21.3	21.4
70 : 30	13.9	-	13.9
50 : 50	9.6	9.6	9.6
30 : 70	8.4	8.3	8.4
10 : 90	7.6	7.6	7.6
1: 99	7.1	7.4	7.2
0: 100	6.5	6.7	6.6
* 0 : 100	6.7	7.1	6.9
0 : 100	7.1	6.8	7.0

* given in Report No 1

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7. Aqueous solution of MgSO_4 - H_2SO_4 system (30°C)

Concentration and molecular ratio	solubility of PbSO_4 in mg/l		
	supernatant method (skimming)	filtration method	average
MgSO_4 : H_2SO_4			
100 : 0	5.5	-	5.5
100 : 0	5.6	5.5	5.6
99 : 1	10.0	9.9	10.0
90 : 10	10.0	9.7	9.9
70 : 30	8.0	-	8.0
50 : 50	5.4	5.4	5.4
30 : 70	6.8	6.6	6.6
10 : 90	8.9	-	8.9
1 : 99	9.5	9.7	9.6
0 : 100*			6.6
			6.9
			7.0

*given in Report 1

Solubility of PbSO_4 in MgSO_4 - H_2SO_4 aqueous solution MgSO_4 : H_2SO_4 mol ratio- 12 -
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The $\text{MgSO}_4 - \text{H}_2\text{SO}_4$ solubility curve and also that of $\text{MgSO}_4 - \text{H}_2\text{SO}_4$ both show two maximums.

8. Aqueous solution of $\text{K}_2\text{SO}_4 - \text{H}_2\text{SO}_4$ system (30°C)

The solubility of PbSO_4 in K_2SO_4 solution was extremely slight. This also held true when H_2SO_4 was added.

concentration of solution N/liter		solubility of PbSO_4 (mg/liter)	Remarks
K_2SO_4	H_2SO_4		
1.00	0	approx. 0.1	Nessler's colorimetric tube reading
1.00	0.30	0.2	same as above "formation"
1.00	0.66	" 0.1	same as above solution standard
0.10	9.46	1.7	K_2SO_4 was added to the accum- ulator electrolyte. The method of determining Pb was the ord- inary supernatant method (skimming).
0.40	9.89	1.3	

"Formation" Solution

composition of aqueous solution

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The effect of adding K_2SO_4 to the electrolyte ($1.26 - 1.28 H_2SO_4$)

amount of K_2SO_4 added (N/liter)

CONSIDERATION OF THE RESULTS OF MEASUREMENTS

1. The shape of the solubility curves: there are no curves which show simply decreasing solubility with increasing SO_4 concentration in solution. The curves will show a peak and wave shape with increasing SO_4 concentration. This is doubtlessly due to the activity coefficient of $PbSO_4$. That is, the following relation holds for $PbSO_4$ -saturated system:

a_{PbSO_4} - activity; m - concentration (unit of mol/Kg of H_2O);

γ_{PbSO_4} - activity coefficient; K_{sp} - solubility product

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The maximums and wave-shape in the curve of PbSO_4 's activity coefficient is probably due not only to the SO_4 in the solution but also to changes in influence of the positive ion. The authors obtained a maximum in the curve of solubility in H_2SO_4 (vide Report I), but Croockford did not. The inconsistency in Croockford's findings was shown in Report II.

2. Solvents of considerable solubility

Na_2SO_4 solution indicated the greatest solubility among those solutions tested by the authors. The greater the concentration, the greater the solubility of Na_2SO_4 and its saturated solution reached value: 30 mg/liter (PbSO_4).

The solubility of Na_2SO_4 itself varied considerably at ordinary temperatures, which fact makes Na_2SO_4 somewhat inconvenient to use as a "formation" solution.

If H_2SO_4 is added to Na_2SO_4 the solubility PbSO_4 decreases. $(\text{NH}_4)_2\text{SO}_4$ gives the highest solubility after Na_2SO_4 .

3. Two-component Solvents

When a part of the positive ions is replaced with H^+ , the solubility of PbSO_4 generally decreases for fixed SO_4^{2-} ion concentration of the sulphates. Precisely speaking, however, maximums in the solubility curve are generally indicated at a certain phase during H^+ replacement. The is especially true in the case of MgSO_4 . A very sharp maximum is indicated in the solubility curve of PbSO_4 when a small amount of MgSO_4 is added to H_2SO_4 or a small amount of H_2SO_4 to MgSO_4 . When the molecular ratio of MgSO_4 : H_2SO_4 is 1:1 the solubility curve indicates a dip or minimum.

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4. Solvents of slight solubility

When, during "formation" of the negative plate, the solubility of PbSO_4 is slight, the lead crystals formed on the negative plate are small and consequently the capacity of the electrode can be expected to be great, which is in agreement with Jamau's views (Accumulateurs Electriques (1928), 56). Therefore, solvents with slight solubility are worthy of consideration.

According to measurements made by the authors, K_2SO_4 solutions show very small PbSO_4 solubility. However, even K_2SO_4 itself as an alkali sulphate is on the rather small side and thus its conductivity is not great; therefore K_2SO_4 is inconvenient to use as a "formation" solution, which fact necessitates the addition of H_2SO_4 . If K_2SO_4 is 1 N and the H_2SO_4 is 0.66 N, then the unusual characteristics of K_2SO_4 can be maintained and the solubility of PbSO_4 will be only 0.2 mg/liter.

That K_2SO_4 decreases the solubility of PbSO_4 is obviously due to the formation of a double salt. According to M. Barre (Comptes rendus, 149 (1909). 294) this double salt is $\text{PbSO}_4 \cdot \text{K}_2\text{SO}_4$ and when K_2SO_4 is in concentrations greater than the following, than a double salt forms:

Temperature, °C:	7	17	50	75	100
concentration of K_2SO_4 in g/100g	0.562	0.620	1.095	1.373	1.695

Therefore the effect of PbSO_4 's small solubility, when K_2SO_4 is used as the "formation" solution, can be anticipated, as well as the following effects:

PbSO_4 exists as the crystalline double salt $\text{PbSO}_4 \cdot \text{K}_2\text{SO}_4$, but it is reduced during "formation" and becomes crystals Pb; in this case the double salt decomposes and K_2SO_4 returns to the solution. Therefore the variation in molecular volume for the reaction $\text{PbSO}_4 \cdot \text{K}_2\text{SO}_4 \rightarrow \text{Pb}$ is assumed to be considerable.

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The problem of whether these effects on the plates are actually good or bad must be solved in subsequent tests.

CONCLUSIONS

(1) The solubility of PbSO_4 in the following solutions at 30°C was measured:

A) $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_4 , K_2SO_4 , and MgSO_4 for various concentrations up to saturation.

B) $(\text{NH}_4)_2\text{SO}_4\text{-H}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4$, $\text{MgSO}_4\text{-H}_2\text{SO}_4$ where SO_4^{--} of two-component solutions was held fixed at 3 N/liter and/or 4 N/liter.

C) $\text{K}_2\text{SO}_4\text{-H}_2\text{SO}_4$ solutions; one having an addition of a small amount of H_2SO_4 to K_2SO_4 , the other a small addition of K_2SO_4 to H_2SO_4 .

(2) Among the above solutions, Na_2SO_4 produced the greatest solubility while K_2SO_4 produced the least.

(3) The value of "formation" solutions for lead accumulators was discussed.

This research was concluded in March 1938. At this time KUKUMOTO Tsutomu was a student at the Academy and had been transferred to this laboratory from the YUASA Accumulator Manufacturing Company.

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